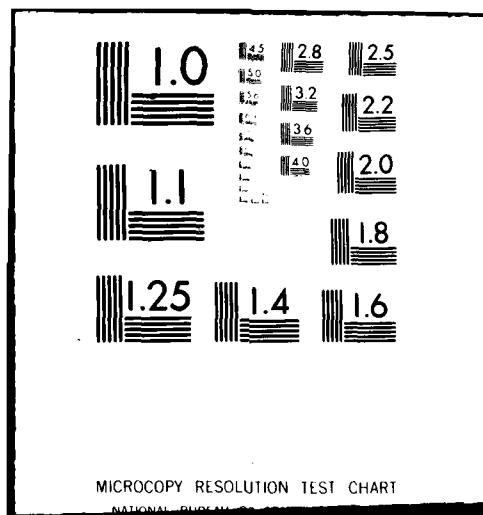


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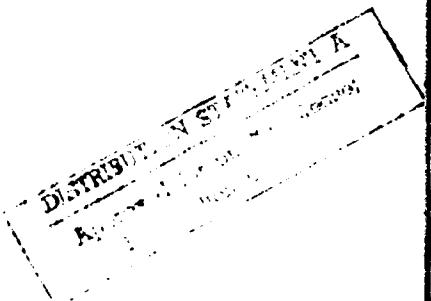
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>A green thin film electroluminescent emitter has been developed capable of greater than 700 fL brightness. This is the brightest green EL device reported to date. The device is a multi-layer structure consisting of ZnS:TbF ₃ layer sandwiched between two dielectric layers of Y ₂ O ₃ . F		



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1.0 SUMMARY

The objective of this program was to evaluate the feasibility of incorporating rare-earth fluorides into a thin film ZnS matrix in order to fabricate a multi-color EL display. Terbium fluoride (TbF_3) was chosen as the initial material to investigate. Described in this report are the results of characterizing these thin film emitters. The characterization included (1) optical spectrum, (2) brightness-voltage-efficiency curves, (3) decay measurements, and (4) annealing experiments.

In summary, the results show that a green emitting thin film EL device capable of producing a brightness of 700 fL was observed. This is the first time such a high brightness green emitting device has been reported. These high brightness, long lived thin film EL emitters exhibit many of the characteristics required for a flat panel TV matrix display for military applications (e.g., immunity to ambient extremes of light, shock, vibration, temperature, nonlinear electro-optic response for matrix address, adequate time response to pulse excitation and low power consumption).



2.0 BACKGROUND

The objective of this program is to investigate multi-color thin film electro-luminescent devices using various rare-earth fluorides as activators. The goal of the first phase of the program involved evaluating TbF_3 as an activator in a ZnS matrix to create a green emitting thin films device. In the next phase of the program we will investigate the rare-earth activator Europium fluoride (EuF_3). This material can be incorporated in the ZnS lattice as either Eu^{+2} or Eu^{+3} . The Eu^{+2} emits in the blue and the Eu^{+3} in the red.

The most efficient thin-film phosphor system reported to date is manganese-activated zinc sulfide (5 lm/W).¹ The Mn^{+2} ion is incorporated substitutionally for zinc in the zinc sulfide lattice. Concentrations of 1-2% Mn give optimal performance. Luminescence is caused by impact excitation of the Mn^{+2} ion. The decay time and color spectrum is determined by electronic transitions in the Mn^{+2} ion. The resultant emission spectrum is relatively broadband peaked at 5800 Å (yellow) and also includes a weaker green and red component. The emission spectrum of Mn^{+2} is due to states internal to the manganese ion and therefore makes it less affected by the external ambient (temperature, electric field strength or frequency, host lattice impurities).

The rare-earth activators also exhibit emission from states internal to the ion and should therefore have characteristics similar to manganese activated films. In addition rare-earth activators (Eu^{+2} , Eu^{+3} , Tb^{+3}) have provided the most efficient visible conversion for lamp phosphors.² It has



been reported that TbF_3 is the most efficient of the rare-earth activators for thin film emitters. The emission is peaked at 5425 Å (green). Recent reports in the literature indicate device capable of 200 fL brightness with 0.3 lm/W efficiency.³

The approach taken under this program utilized fabrication techniques developed at this laboratory which have yielded high brightness long-life thin film emitters using Mn activated ZnS. These films have the highest efficiencies reported to date (5 lm/W). These fabrication techniques have allowed us to produce ZnS films doped with TbF_3 , which have a brightness of greater than 700 fL and efficiencies of 0.2 lm/W; these are the brightest thin film electroluminescent devices using an activator other than Mn reported to date.

It has been reported that incorporating the rare-earth as molecules of rare-earth fluorides increases the stability of the light emission of the films.⁴ Rare-earth activators characteristically have narrowband emission spectra since the optical transition involves shielded inner shell electrons of the rare-earth ion so that effects of the host lattice are minimized. Therefore, the emission is relatively independent of temperature and frequency compared to other types of activators. This is an important consideration for a matrix addressed display operating over a wide temperature range since many frequency components are present in the matrix address system.



3.0 MATERIALS FABRICATION

The rare-earth activated ZnS films are made using the same fabrication techniques as used to make the high brightness, high efficiency Mn activated films. This consists of a "hot wall" electron beam evaporation system which is microprocessor controlled. The activator is introduced by co-evaporation which is done in a resistance-heated boat. The thickness of the film is monitored with a laser monitor during deposition. The substrate is maintained at an elevated temperature through the use of quartz lamps in the vacuum chamber.

The films are fabricated on Corning glass 7059 coated with indium tin oxide. The structure which is shown in Fig. 1 consists of a transparent conductor, a layer of Y_2O_3 followed by a layer of ZnS doped with the appropriate activator, a second layer of Y_2O_3 followed by a conductor such as aluminum.

It has been found that in order to obtain optimum electroluminescence with the Mn film, it is necessary to anneal the films at an elevated temperature for about an hour. Films which are not annealed have a very low light output. This anneal procedure causes the manganese to redistribute to the proper site. Also the annealing improves the crystallization of ZnS.⁵ This procedure has been optimized for Mn activated emitters as evidenced by the highest efficiency reported to date.¹



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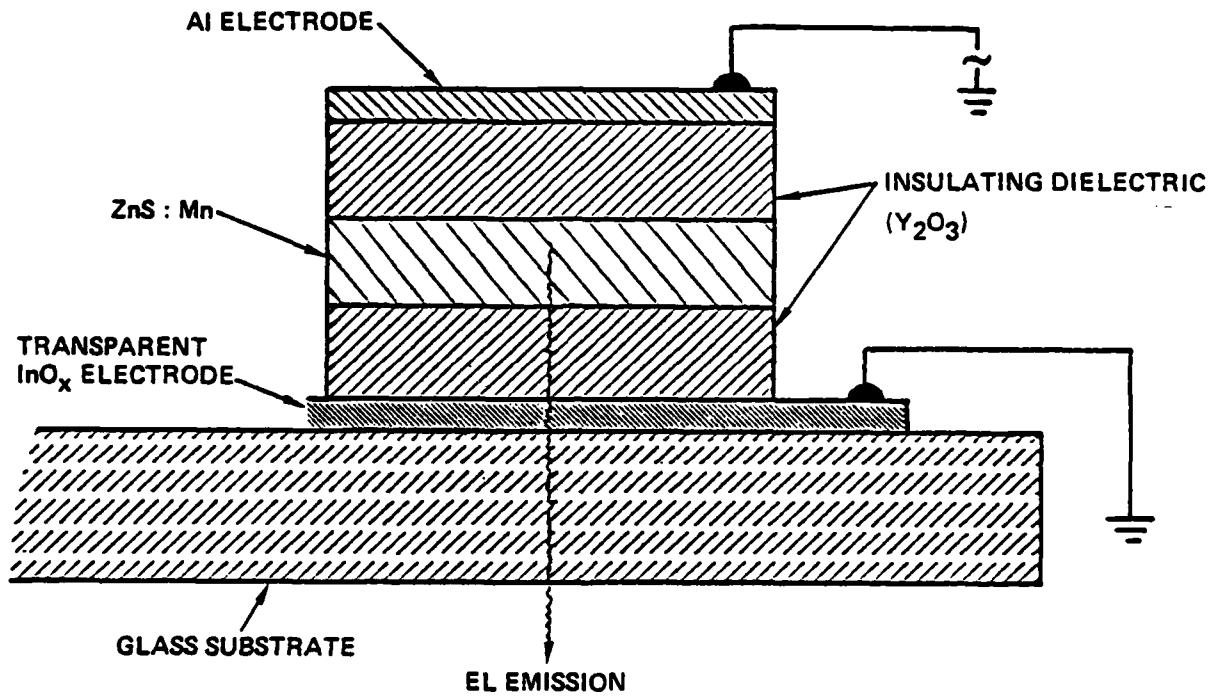


Fig. 1 Thin film emitter structure.



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Preliminary results with the Tb activator indicate that the unannealed films are capable of emitting over 300 fL while the annealed samples were capable of emitting over 700 fL.



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4.0 ELECTRO-OPTIC MEASUREMENTS

Several electro-optic measurements are made on the thin film emitters: (1) the emission spectrum is made using Jarrel Ash 1/2 meter monochromator and PAR lock-in amplifier, (2) the brightness vs voltage and the luminous conversion efficiency are measured using an HP 3052A data acquisition system. The activator concentration is determined using energy dispersive x-ray analysis (EDAX). Also the instantaneous decay time constants were determined from the oscilloscope trace.

The room temperature electroluminescence spectrum is shown in Fig. 2. This spectrum has not been corrected for photomultiplier response. The spectrum has the characteristic appearance associated with ZnS:TbF₃ films reported in the literature.⁴ However, there are some differences. A comparison of the two spectra in Fig. 2 shows the influence of the fluorine ion. The presence of the fluorine appears to have the greatest influence of the electric dipole transitions ($^5D_3 + ^7F_5$, $^5D_4 + ^7F_6$). These transitions are normally forbidden. However the influence of the crystal field relaxes the selection rule. The goal is to make a thin film emitter with a narrowband emission of a single wavelength. Incorporating TbF₃ instead of Tb metal into the ZnS matrix appears to be approaching this. The $^5D_4 + ^7F_6$ (4890 Å) is a forbidden electric dipole transition which is probably vibronically induced. The activator (TbF₃) used in these films is the same as used in the P43 CRT phosphor. This spectrum also differs from that reported by Okamoto and Hamakawa. Their spectrum indicates much larger peaks for the low energy



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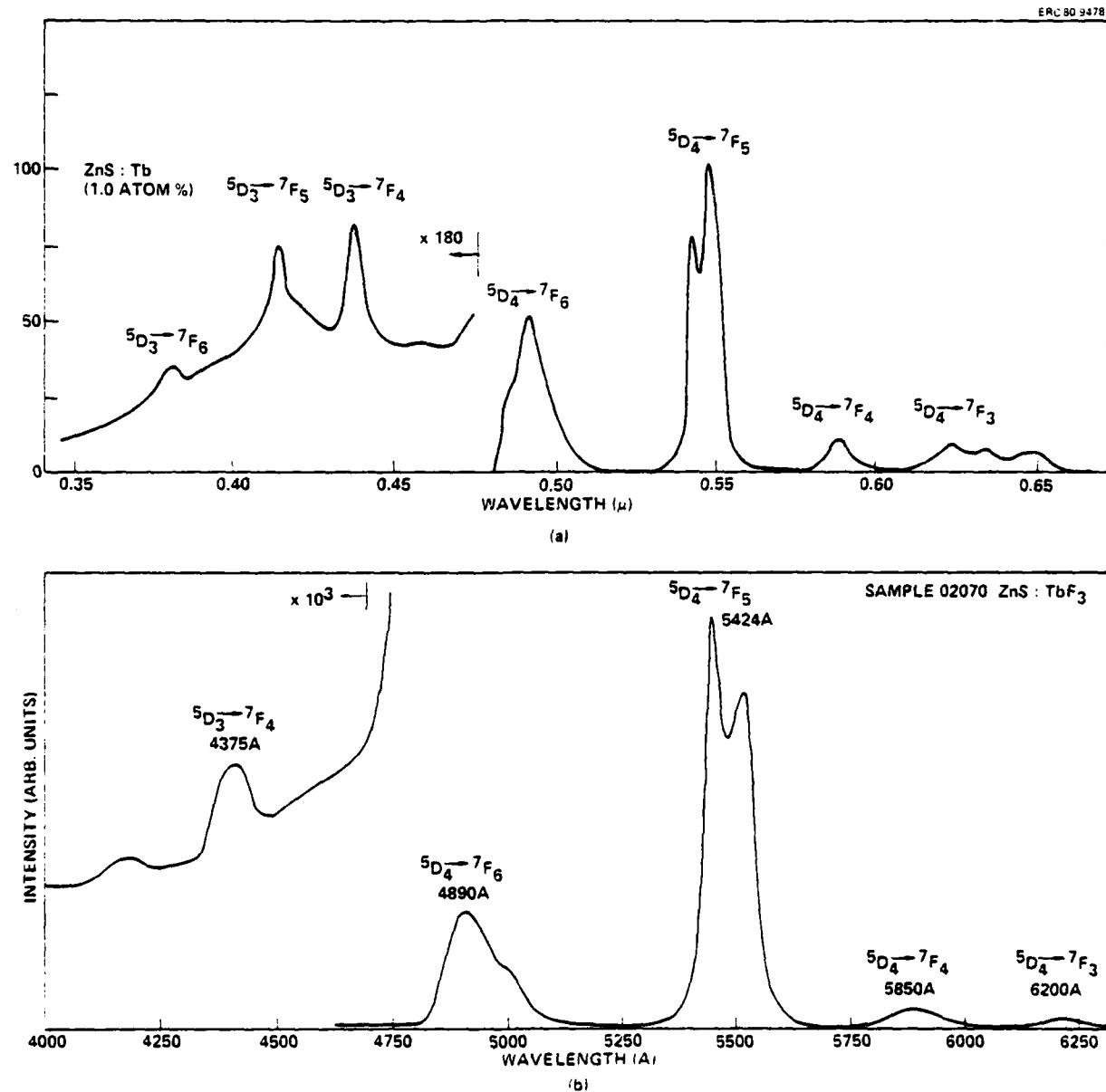


Fig. 2 Room temperature thin film electroluminescence spectrum
(a) ZnS:Tb; (b) ZnS:TbF₃.



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lines ($^5D_4 + ^7F_4$, 5840 Å, $^5D_4 + ^7F_3$, 6190 Å). A series of experiments were performed in which the intensities of the 4385 Å line ($^5D_3 + ^7F_4$), the 4890 Å line ($^5D_4 + ^7F_6$) and the 5425 Å line ($^5D_4 + ^7F_5$) were measured as a function of voltage. The ratio of the $^5D_4 + ^7F_6$ to the $^5D_4 + ^7F_5$ remained constant, while the ratio $^5D_3 + ^7F_4/ ^5D_4 + ^7F_6$ decreased with voltage (see Fig. 3). It might be expected that as the field across the ZnS increases the energy the electrons gain increases, which in turn would increase the number of excitations to the higher energy 5D_3 level. If these decayed radiatively to the ground state then the ratio of $^5D_3 + ^7F_4/ ^5D_4 + ^7F_6$ would increase with field. Since this ratio decreases there must be a significant number of nonradiative transitions from the 5D_3 to the 5D_4 level. This would increase the number of transitions from the $^5D_4 + ^7F_6$ (4890 Å) and $^5D_4 + ^7F_5$ (5425 Å) level.

Brightness vs voltage measurements are made with a calculator controlled data acquisition system. Figure 4 shows a typical B-V curve for a Tb activated ZnS layer. Also shown in Fig. 4 are the most recently published report of thin film ZnS:TbF₃ by Okamoto et al. The films developed under this contract have a maximum brightness 3-1/2 times greater and a peak drive voltage that is 1.7 times lower. It should be noted that the brightness is plotted on a log scale. The steep non-linear response indicates that the same mechanism responsible for emission in Mn activated devices is dominant in the Tb devices. This mechanism can be explained as follows: charges from deep traps within the active layer are field ionized and swept to the interface between the dielectric(Y₂O₃) and the ZnS layer where they are trapped. In the



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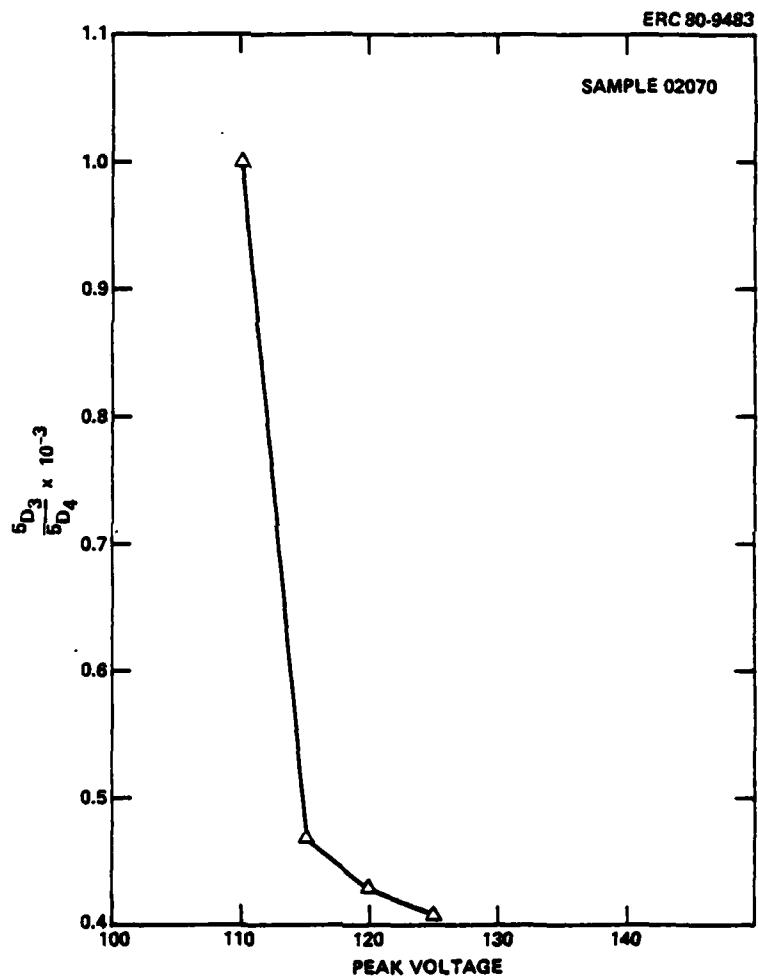


Fig. 3 Ratio of $5D_3$ to $5D_4$ transitions for $ZnS:TbF_3$.



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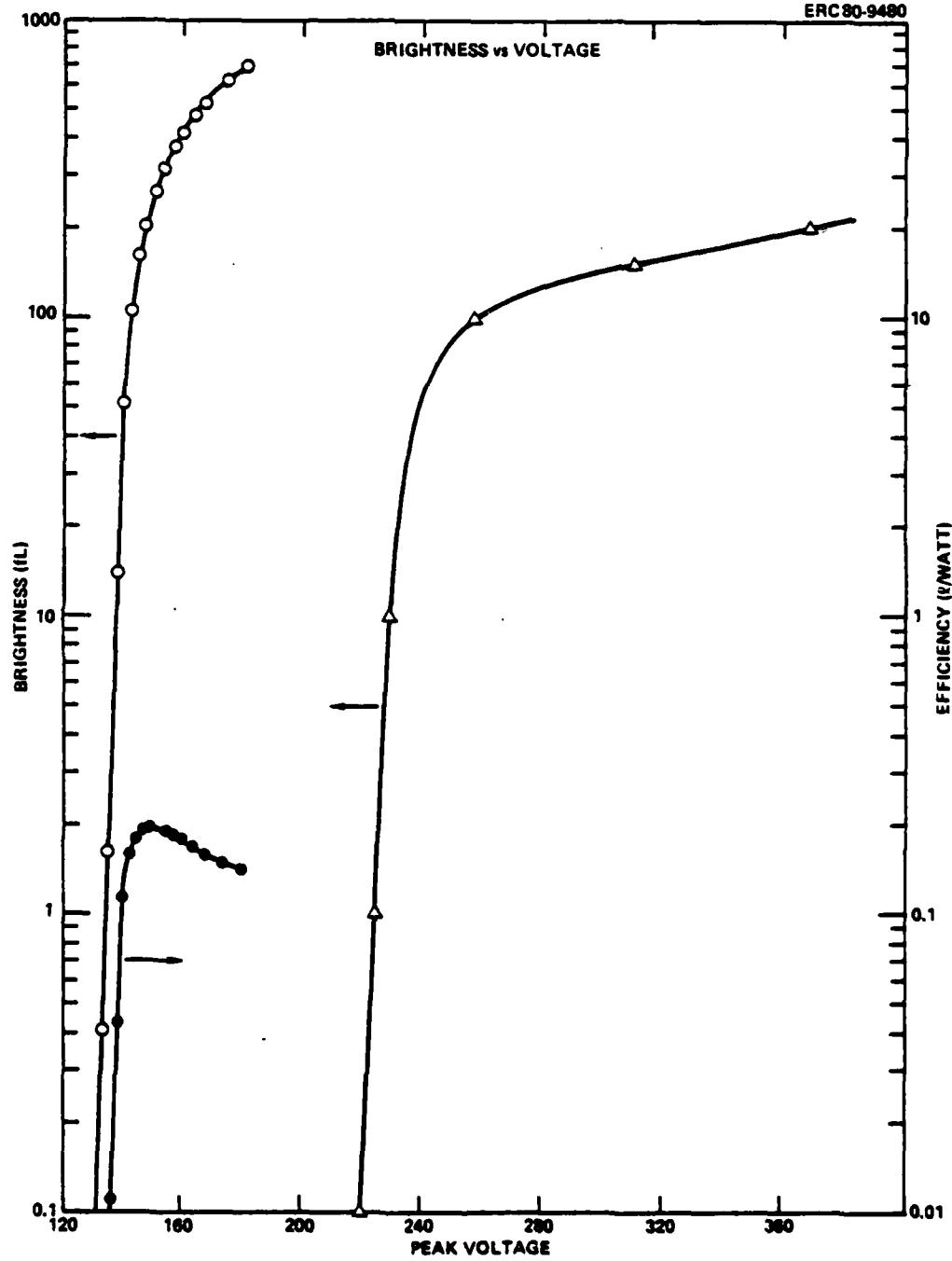


Fig. 4 Results of this program compared to published results.
○ Rockwell ●, △ Okamoto, et al.



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next voltage cycle they remain in their traps until the field reaches a sufficient level to allow the charges to tunnel through the barrier and become "hot electrons" very fast. These energetic electrons then impact excite the activator causing luminescence and are trapped at the opposite interface where they remain until the next half cycle of the voltage waveform. The process then repeats itself. It is this tunneling field emission which explains the steep non-linear characteristics of these thin film emitters.

Electron injection by tunnel emission into the ZnS provides a distinctly different electro-optic response for thin film emitters compared with previous devices using bulk powder phosphors. Tunnel emission is insensitive to temperature and is sharply dependent on electric field strength. The expression for the current density is

$$j(t) = n_1 v(E_1) e^{-AE_1^{2/3}/F}$$

n_1 = density of electrons in trap E_1

v = vibrational frequency of electrons in traps

E_1 = energy of trapping level

F = electric field across active layer

A = constant.

The brightness which is proportional to the tunneling current, therefore, is very nonlinear with respect to the voltage on the device. The validity of the model for Mn activated films has been reported previously.⁶



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Figure 5 shows a plot of $\log j_{\max}$ vs $1/F$ for a Tb activated sample. The electronic current is found by placing a triangular voltage waveform across the device and monitoring the current. For a capacitor which exhibits no tunneling, the current waveform is a square wave. However, for a device in which there is a tunneling current this current is superimposed on top of the square wave displacement current (see Fig. 6). The slope of the $\log j_{\max}$ vs $1/F$ curves gives the energy of the trap level. It can be seen from the figure that there appears to be two slopes. The bending of the curve at higher voltages is due to polarization charge which is building up at the opposite interface. This polarization produces a field which opposes the internal field across the active layer. As the external field is increased a larger proportion is dropped across the dielectric.

The number of charges which appear at the opposite interface can be determined by integrating under the electronic current waveform. The change in field due to these charges is sufficient to cause the change in slope of the j_{\max} vs $1/F$ curve. Further evidence which shows that the polarization charge is responsible for the change in slope is seen in Fig. 5 where the frequency has been increased to 5 kHz and the change in slope is less. Similar results have been reported by this laboratory in the past for Mn films.⁷

The luminous conversion efficiency is also shown in the same Fig. 4. The efficiency is determined by sampling the voltage waveform across the device and the current through the device. The instantaneous power consumed by the device is calculated by integrating the two functions over the



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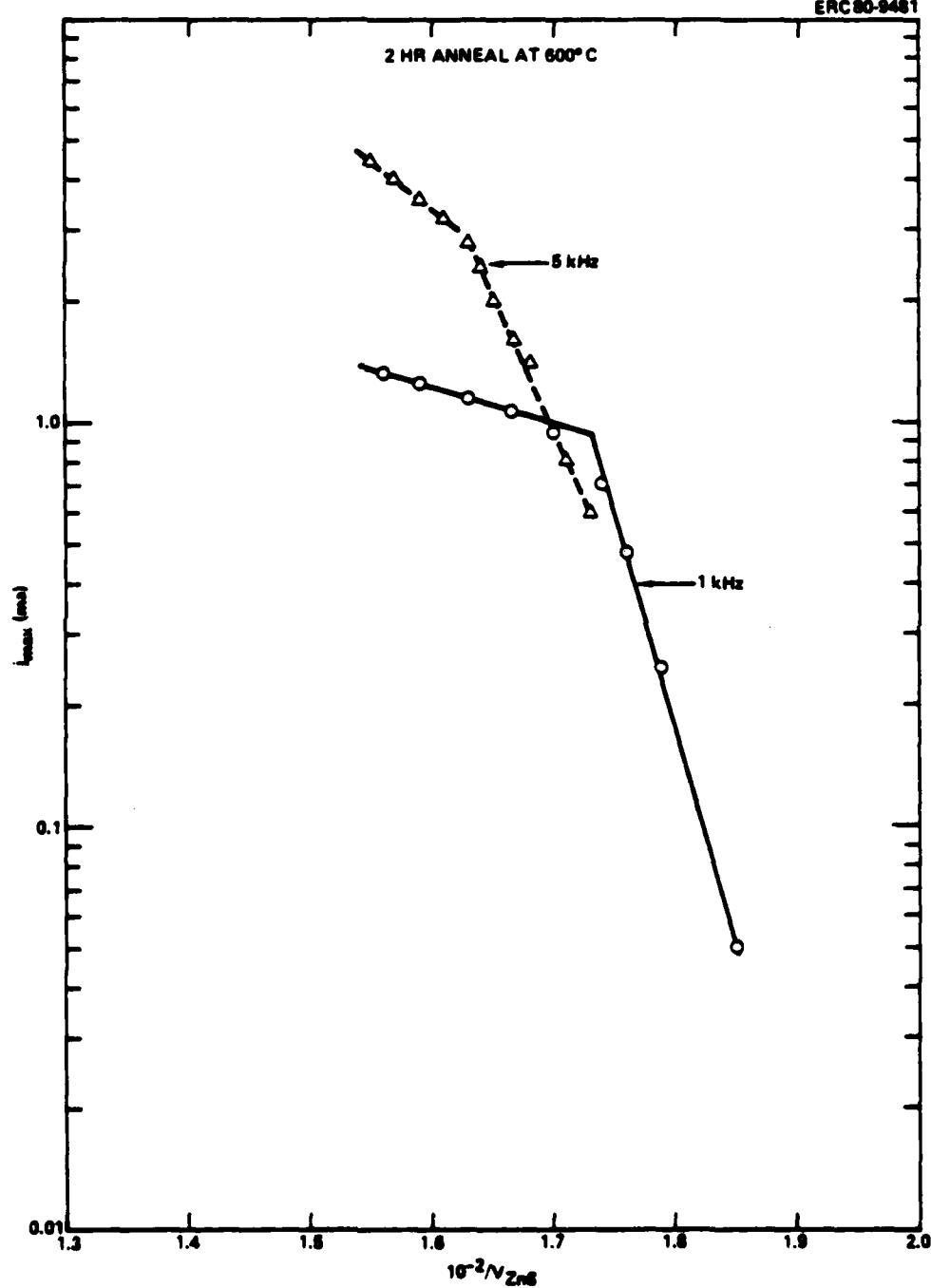


Fig. 5 Electronic current vs $(\text{field across ZnS})^{-1}$ for ZnS:TbF_3 thin film.



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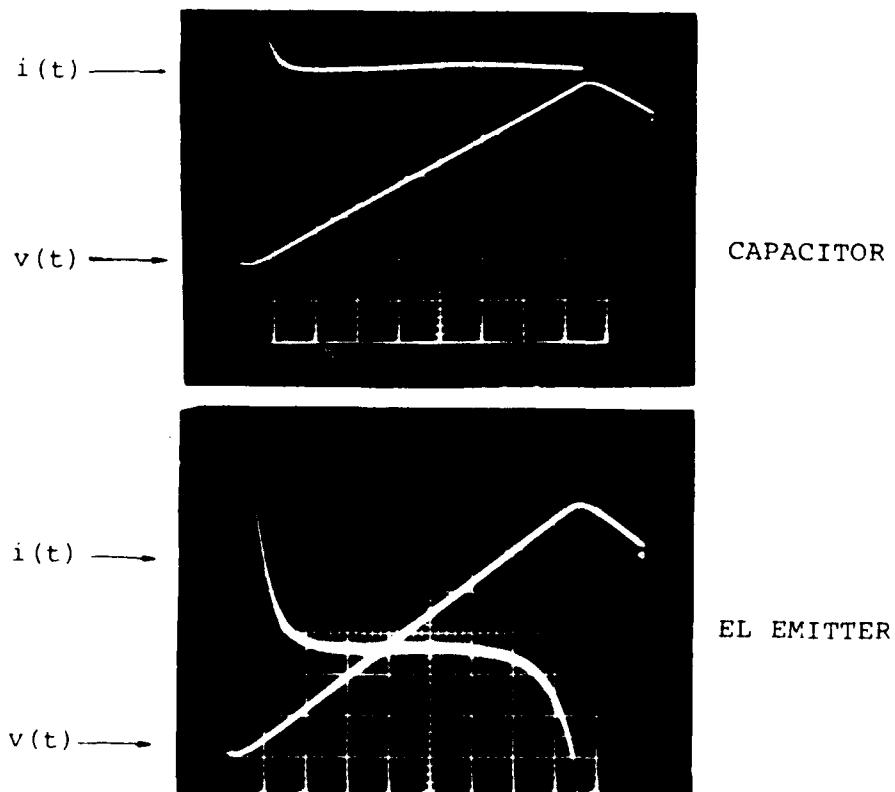


Fig. 6 Technique for separating electronic current from displacement current.



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period of the waveform. The luminous conversion efficiency is then calculated knowing the average brightness and the area of the emitter. This is all accomplished with the HP 9825 calculator.

Figure 7 shows the decay characteristics of a typical Tb activated EL film. The luminescence decay consists of at least two exponential components. This has been explained in the literature as due to the formation of activator complexes as the concentration is increased. The longer time constant is associated with isolated activator centers and the faster time constant associated with complexes.⁵ This is particularly true for manganese activated thin films and also appears possible for the terbium films. Further work is needed in this area. If complexes are being formed as the activator concentration is increasing, this is probably influencing the maximum efficiency. The time at which the intensity falls to 1/e of its initial value is 380 μ s. Previously reported values were 220 μ s Chen et al and 700 μ s Okamoto et al. The decay time of a Mn activated film is included in Fig. 7 as a comparison.

Figure 8a, b, c, d shows the effect of annealing a device at constant temperature for different times. The plots show that the luminous conversion efficiency remained constant whether the device was annealed or not. The fact that the two hour anneal increased the maximum light out and current density indicates that this particular time-temperature cycle increased the number of charges available to produce light. However, since the conversion efficiency



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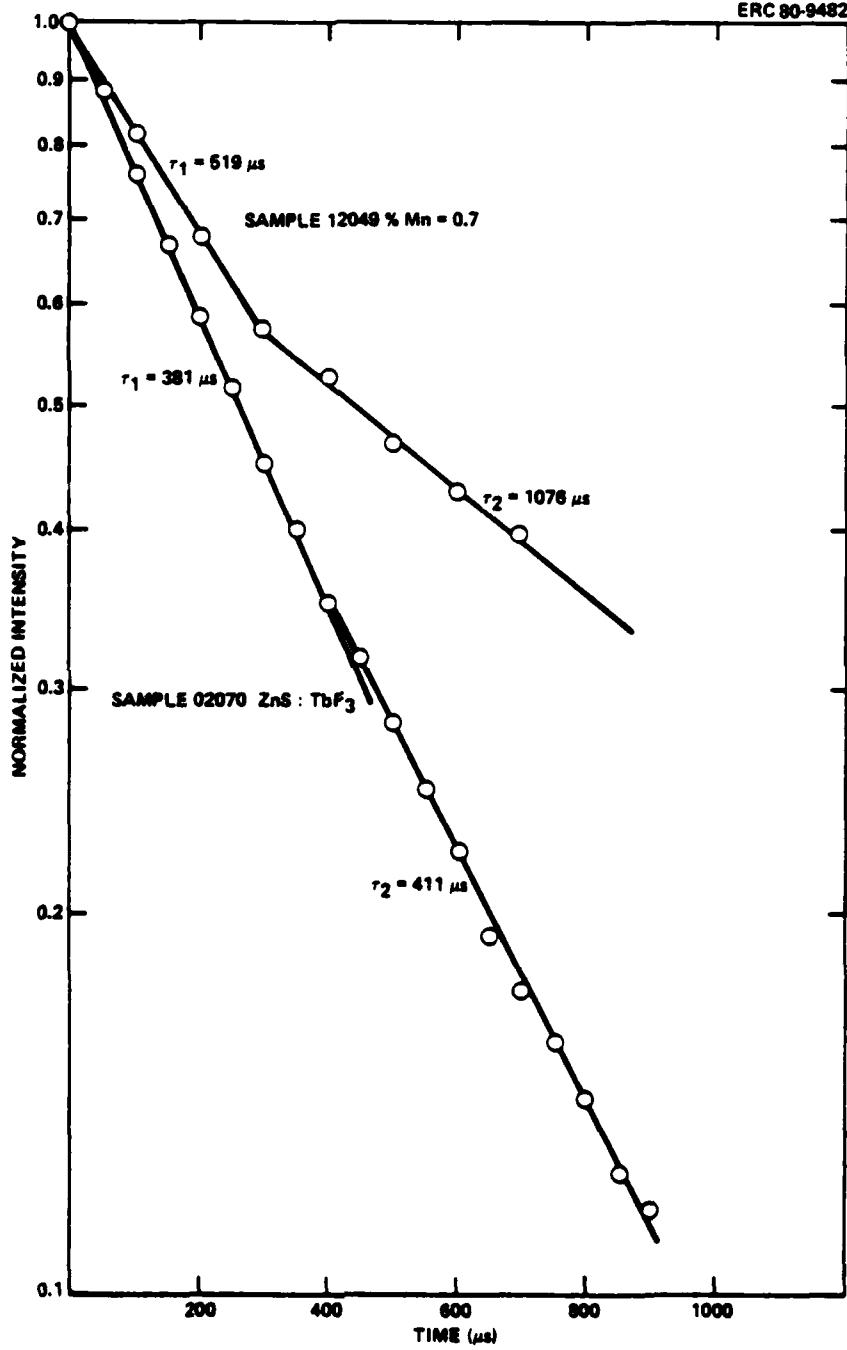


Fig. 7 Brightness vs decay time for Tb and Mn activated EL film.



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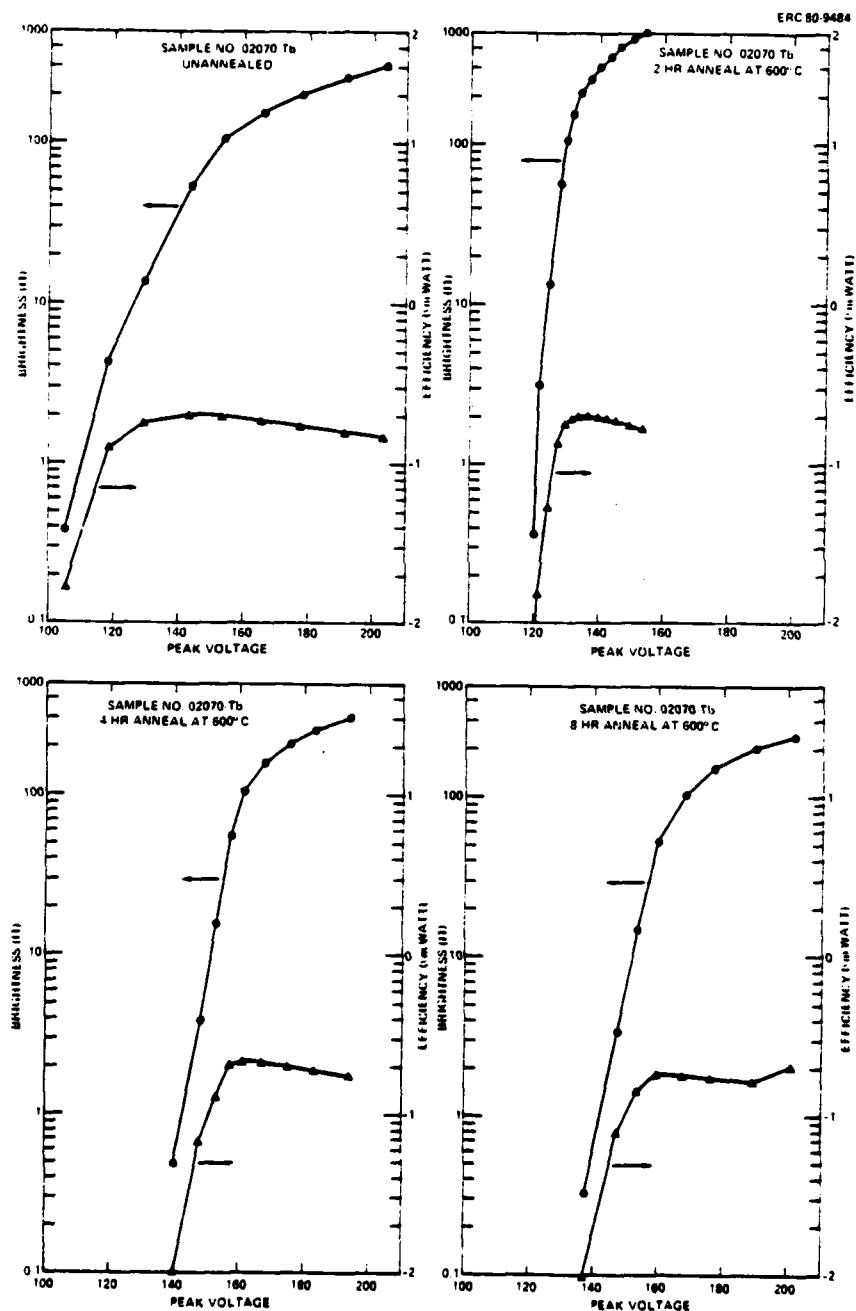


Fig. 8 Effect of annealing at constant temperature for different times.



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did not change the non-radiative decay mechanisms were not affected. This implies there is a better anneal temperature since results with Mn activated films indicates that annealing improves both the maximum light out and the efficiency. With the Mn films annealing tends to make the film more crystalline which increases the mean free path of the hot electron. The maximum power efficiency is determined by the product of the electric field across the active layer and the mean free path of the electron.⁸ Electron spin resonance experiments done at this laboratory has shown that annealing Mn activated films causes localized Mn⁺² ion to diffuse so that they are more homogeneously distributed in the lattice.

Additional anneal time-temperature cycles should be investigated fully to optimize the effect of this parameter on the brightness and efficiency.



5.0 CONCLUSION

A bright green thin film electroluminescent device has been developed using $ZnS:TbF_3$ as the active layer. Using fabrication techniques developed for high efficiency Mn activated ZnS films have allowed us to fabricate the brightest green emitter (700 fL) reported to date. The mechanism for excitation appears to be the same as for the Mn film, that is tunnel field emission. The spectrum is the same as reported in the literature except that more emission appears in the green 5425 \AA ($^5D_4 \rightarrow ^7F_5$) line. The ability to generate high brightness films is strongly dependent on the anneal cycle performed after deposition. Further work needs to be done in this area in order to optimize the performance of the films. Decay measurements indicate that there may be some clustering of the Tb^{+3} ions for this particular concentration (~ 5 weight per-cent). Films with various concentrations need to be investigated to further understand this phenomenon. An investigation in the optimization of the anneal cycle would improve the efficiency.



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